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Ultrafast vibrational spectroscopy (2D-IR) of anions in ionic liquids

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Ionic liquids hold promise for applications in energy storage as the electrolyte in electric double-layer capacitors and other devices. Further optimizing device performance through their physical and chemical properties requires an improved understanding of the detailed interactions between cation and anion and how they reorganize in the presence of charge. Here we probe the dynamics of thiocyanate ions in several bulk imidazolium bis(trifluoromethylsulfonyl)amide ionic liquids from femtoseconds to 100 ps using ultrafast vibrational spectroscopy. Two-dimensional infrared (2D-IR) spectroscopy of thiocyanate ions detect both inertial motion (on the hundreds of femtosecond timescale) as well as slower, diffusive motions (on the tens of picosecond timescale). The 2D-IR experiments show that the rate of fluctuation of the electrostatic environment around the thiocyanate is sensitive to hydrogen bonding at the 2-position of the imidazolium ring. The correspondence of time-scales with molecular dynamics simulations suggests that the picosecond motions we observe are fluctuations around a local free-energy minimum while the tens of picoseconds timescales correspond to the rearrangement of those local intermolecular arrangements. Our measurements implicate the break-up of local ion cages as the activating event for the onset of translational motions which are responsible for viscosity and conductivity. We additionally test our hypothesis that the SCN⁻ anion is sensitive to the local environment by introducing co-solutes – counter-cations such as K⁺ and water. We observe contact-ion pairs, i.e., SCN⁻ anions with a K⁺ counter charge in the first solvation shell through a static component in the frequency correlation function. We observe water-bound SCN⁻ through changes in linewidth, population relaxation rates, and dynamics. The SCN⁻ is an eloquent reporter of local structure and dynamics in these complex fluids.